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EXHIBIT A

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A REGIONAL TECHNICAL CONFERENCE SPONSORED BY THE
Color & Appearance Division
and the
St. Louis Section of the Society of Plastics Engineers

Promoting the Science of Coloring Plastics

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The Effect of IR Reflecting Black Pigment Selection on Weatherable R-PVC

Introduction:

IR Reflecting Black pigments are commonly used in R-PVC applications where excellent weatherability and low "heat build-up" are primary requirements. A few of the application areas with these requirements are vinyl siding and vinyl window profiles. In both of these areas, the color hold or weatherability and the degree of heat build-up are key factors in the products performance. It has been well documented that the IR reflecting black pigments give superior performance with regard to heat build-up over other alternate black pigments (Carbon Black, Copper chromes, ...).

Within the IR reflecting black pigments, essentially three basic types with regard to color and composition can be defined. One area is covered by Pigment Black 30's - CrFeNiMn (approx. 18% as Fe), which are typically blue/green in shade. The other two types are both classified as [1]Pigment Green 17's (CrFe) which differ with respect to the Cr:Fe ratio. The two regions can be classified as approximately 11% Fe containing pigments, which are in the red/yellow color space and approximately 34% Fe containing pigments, which are red/blue in shade(Figure 1). The aim of this paper is to try to differentiate the performance of the three black pigment ranges as individual pigments and in a few typical vinyl siding shades.

The Design: (also see the "General Information" attachment)

Although, IR Reflecting black pigments are the primary pigment used in gray vinyl siding shades, they are used more often in combination with C.I. Pigment Brown 24's(CrSbTi's) & C.I. Pigment Yellow 164's(MnSbTi's) to make a wide variety of shades. The design of this study is to look at the heat build-up and weathering of the individual black pigments(gray) and to also evaluate their performance in a few typical siding shades - light, medium, and dark beige(Figures 2 - 4).

The R-PVC compound used for this report is Tin Mercaptide stabilized and contains 10phr TiO_2. All IR Reflecting black pigments used are commercially available codes with one C.I. Pigment Black 30(~18% Fe) and one C.I. Pigment Green 17(~34% Fe) being used. However, since there is a wider range of pigments in the C.I. Pigment Green 17, "low Fe" area that vary somewhat in both % Fe content and shade, the results reported for C.I. Pigment Green 17(~11% Fe) are average values from three commercially available grades.

The light, medium, and dark beige shades results reported are averages of a number of color matches where the match consisted of combination of an IR Reflecting black pigment, a C.I. Pigment Yellow 164 and a C.I. Pigment Brown 24. Chrome oxide green was used as a shading component when necessary. The IR reflecting black and C.I Brown 24 pigments for each match were varied, while a single C.I. Yellow 164 pigment was used in all matches. In compiling the results, the C.I. Brown 24 pigments used showed very little variation with regard to IR

[1]It should be noted that some commercially available pigments considered as C.I. Pigment Green 17's in this paper are classified as C.I. Pigment Brown 35's according to their manufacturers.

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reflectance and weathering performance. Therefore, although a number of commercially available CrSbTi's were used, they were considered for reporting purposes to be a single pigment.

All weathering results were from South Florida outdoor weathering - ASTM #G7-89 guidelines were followed. The % IR reflectance was measured on a Datacolor CS9000 spectrophotometer. Heat build-up results were compiled using a Cerdec designed unit, which does not conform to the ASTM D4803 specification. Therefore the heat build-up results are used for relative comparisons only.

The Results:

In looking at the individual black pigment types, some clear differences are apparent. The Pigment Black 30 contains ~18% Fe, while the two Pigment Green 17's contain ~11 and ~34% Fe, respectively(General Info. attachment). The IR reflectance/Heat build-up results(Figures 5 - 12) on the individual black pigment types show that the Pigment Black 30 has lower % IR Reflectance by approximately 10 - 20% than either of the Pigment Green 17's and therefore a higher degree of heat build-up, 10 - 15°C. The one year South Florida weathering results(Figure 13) show that the Pigment Black 30 is weathering the best at this stage, followed by the ~11% Fe containing C.I. Pigment Green 17, and the poorest weathering is exhibited by the ~34% Fe containing black. Since Fe is well known to have a deleterious effect on R-PVC, these results are not surprising.

For the "matched shades" the % IR Reflectance and heat build-up results show exactly the same trends as seen with the individual black pigments(Figures 7, 9, & 11). However, it is very important to note that the relative differences for both IR Reflectance & Heat Build-up between the matched shades based on the different IR Reflecting black pigments are much smaller than for the individual black pigments. Since Pigment Brown 24 and Pigment Yellow 164 both have higher IR reflectance than any of the IR reflecting blacks the net differences in both % IR Reflectance and Heat Build-up of the matched shades is greatly reduced.

The overall South Florida weathering results on the matched shades show that, again, the Pigment Black 30 based matches give the best weathering results(Figure 14). However, it is interesting to note there is a reversal of the relative weathering results between the Pigment Green 17 type blacks. The matches based on the ~34% Fe containing black, although slightly poorer than the Pigment Black 30 based shades, are are performing better than the matches based on the ~11% Fe containing black pigment. This reversal can not be explained by looking at the average % Fe content of each matched shade(Figure 15). The ~11% Fe containing black matches have a significantly lower Fe content than for the matches based on the ~34% Fe containing black. The one piece of data that shows some correlation to the weathering results on the "beige matches" is the total "parts per hundred weight"(phr) of IR Reflecting black pigment contained in each(Figure 16). These show the Pigment Black 30 based matches contain the least amount of black pigment use, while the matches based on the ~34% Fe containing black show only slightly higher amounts of black pigment use. However, the matches based on ~11% Fe containing black pigment have, by far, the highest loading of black pigment.

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Conclusions/Questions:

1) The heat build-up results show clearly that formulas based on Pigment Black 30 would generally run slightly "hotter" than formulas based on either of the Green 17 type blacks. However, in the color ranges evaluated, the heat build-up differences are relatively small for the "matched shades". One of the most important points to note is that the heat build-up differences seen in this study show no correlation to weatherability.

2) Care should be taken in using weathering of the individual black pigments to predict relative weathering performance of a "matched shade". The weathering results clearly showed that the Green 17 containing ~34% Fe to be the poorest weathering pigment when tested individually, but to have significantly better performance than the 11% Fe containing black when used in making medium and dark beige matches.

3) In trying to determine what factor is influencing the difference in weathering performance of the IR reflecting black pigments, the relative Fe content, surprisingly, showed no correlation to the weathering results. This held true either as individual pigments or in matched shades. As individual pigments the 18% Fe containing Pigment Black 30 showed better weathering results than the ~11% Fe containing Pigment Green 17. In the matched shades, the samples based on the ~34% Fe black pigment contain the highest amounts of Fe. However, the medium and dark beige weathering results clearly showed the shades based on the ~34% Fe black to weather better than the matches based on the ~11% Fe containing black.

4) The best correlation to weathering results is found looking at amount of black pigment used in the matched shades. As the amount of IR Reflecting black pigment increased in both the Medium and Dark beiges, weathering results became poorer. However, although the trend is there, there is not enough data in this study to totally support this theory. One factor not discussed earlier is report is that the Pigment Black 30 crystal is a spinel structure, while the Green 17 crystal is a hematite structure. Obviously not an "Apples to Apples" comparison.

5) Weathering is not an exact science, therefore all work will be both repeated and expanded upon!!!

Future Work:

To advance this work another study will be initiated utilizing a wider range of Pigment Black 30's. Since a number of commercially available versions of this pigment exist which are coloristically identical but differ in tinting strength, it would be expected that medium and beige shades based on the higher strength versions would weather better than the weaker version based on % black pigment content of the final shade. Another factor would be to weather the individual pigments both at equal loading and at equal L* values.

Since it is possible also to vary the shade of Pigment Black 30 from the green/blue shade to a more red/yellow shade, but maintain the identical % Fe content and spinel crystal structure,

pigments of this type will be included to determine the effect of the overall composition and will elimate some of the coloristic differences when comparing the Pigment Black 30 chemistry Green 17 types.

Acknowledgements:

The author would like to thank B. Bier who spent many hours preparing and evaluating the weathering plaques, G. Rangos & Dr. D. Swiler for their technical guidance and assistance, and Cerdec Corporation for the permission to publish this paper.

References:

Predicting Heat Buildup in PVC Building Products, ASTM D4803-89, American Society for Testing Materials, Philadelphia, PA

Practice for Atmospheric Environmental Exposure Testing of Nonmetallic Materials, G7-89, American Society for Testing Materials, Philadelphia, PA

[redacted]

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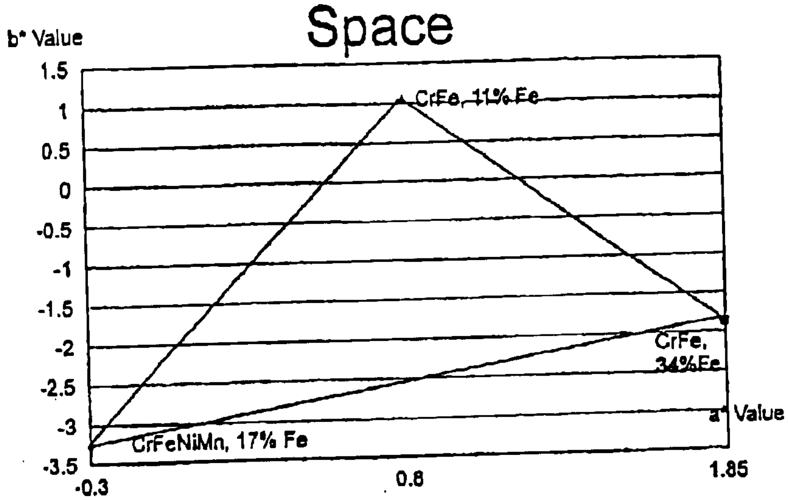
IR Reflecting Blacks - Color Space



CIELAB Ill. D65 @ 10deg., SCI

Figure 1

Light Beige Formulas

Average Composition - In phr

	CrFeNiMn(17% Fe)	CrFe(11% Fe)	CrFe(34% Fe)
Pigment Brown 24(CrSbTi)	0.174	0.149	0.174
Pigment Yellow 164(MnSbTi)	0.035	0.007	
Pigment Black 30(CrFeNiMn)	0.04		
Pigment Green 17(CrFe-11% Fe)		0.072	
Pigment Green 17(CrFe-34% Fe)			0.047
Chrome Oxide Green		0.03	0.006
Total Pigment Loading:	0.249	0.231	0.214

10 phr TiO2 - Matches have DE<0.6 vs. Std.

Figure 2

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Med. Beige Formulas

Average Composition - In phr

	CrFeNiMn(17% Fe)	CrFe(11% Fe)	CrFe(34% Fe)
Pigment Brown 24(CrSbTi)	0.718	0.702	0.881
Pigment Yellow 164(MnSbTi)	0.246	0.127	0.048
Pigment Black 30(CrFeNiMn)	0.173		
Pigment Green 17(CrFe-11% Fe)		0.361	
Pigment Green 17(CrFe-34% Fe)			0.229
Chrome Oxide Green			
Total Pigment Loading:	1.138	1.19	1.158

10 phr TiO2 - Matches have DE<0.6 vs. Std.

Figure 3

Dark Beige Formulas

Average Composition - In phr

	CrFeNiMn(17% Fe)	CrFe(11% Fe)	CrFe(34% Fe)
Pigment Brown 24(CrSbTi)	1.845	1.658	1.91
Pigment Yellow 164(MnSbTi)	0.839	0.314	0.255
Pigment Black 30(CrFeNiMn)	0.744		
Pigment Green 17(CrFe-11% Fe)		1.436	
Pigment Green 17(CrFe-34% Fe)			0.825
Chrome Oxide Green			0.066
Total Pigment Loading:	3.428	3.409	3.056

10 phr TiO2 - Matches have DE<0.6 vs. Std.

Figure 4

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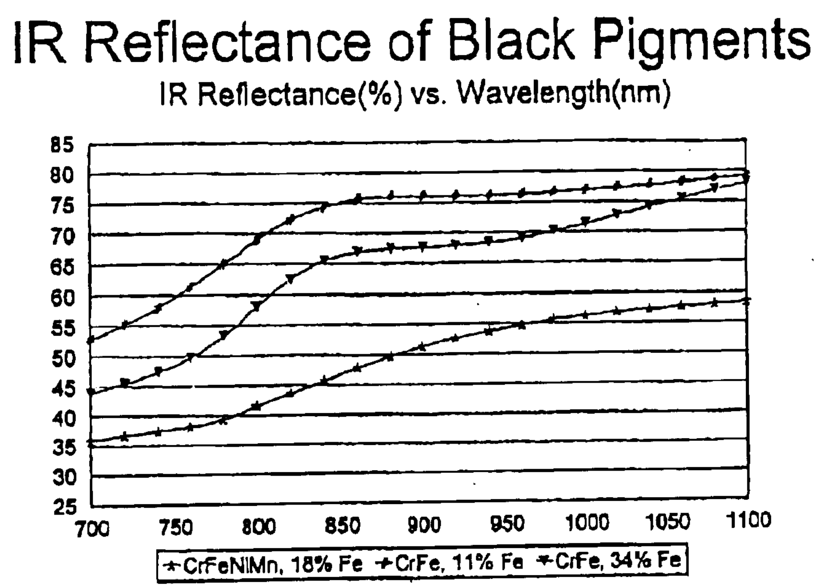
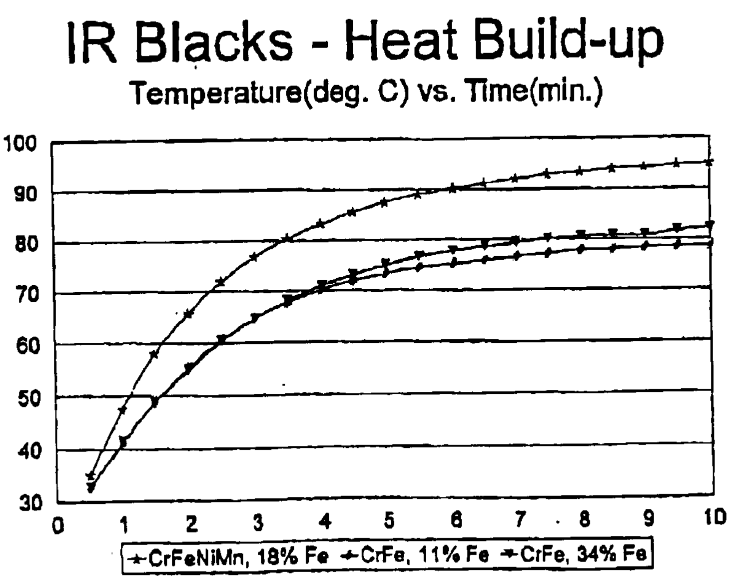


Figure 5

Figure 5



8" bulb height - Equal L* values(67.0+/- 0.5)

Figure 6

IR Reflectance - Light Beiges

IR Reflectance(%) vs. Wavelength(nm)

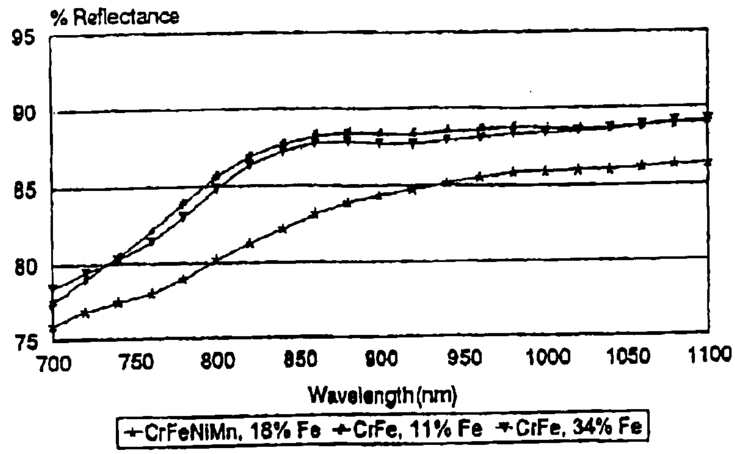


Figure 7

Light Beige Heat Build-up Results

Temp.(Deg. C) vs. Time(min.)

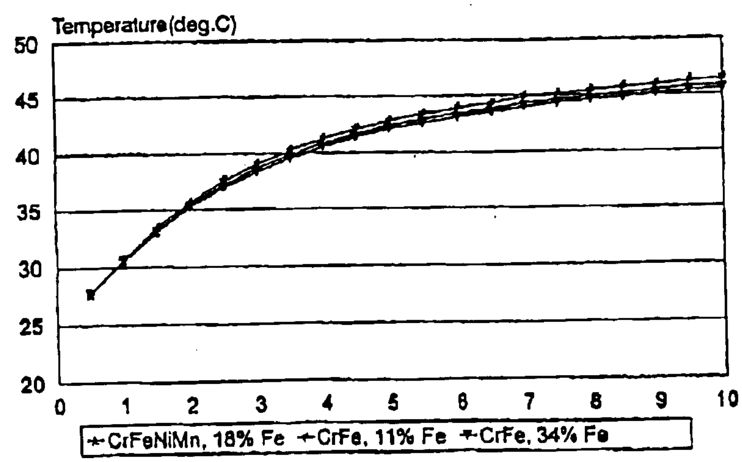


Figure 8

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IR Reflectance - Med. Beiges

IR Reflectance(%) vs. Wavelength(nm)

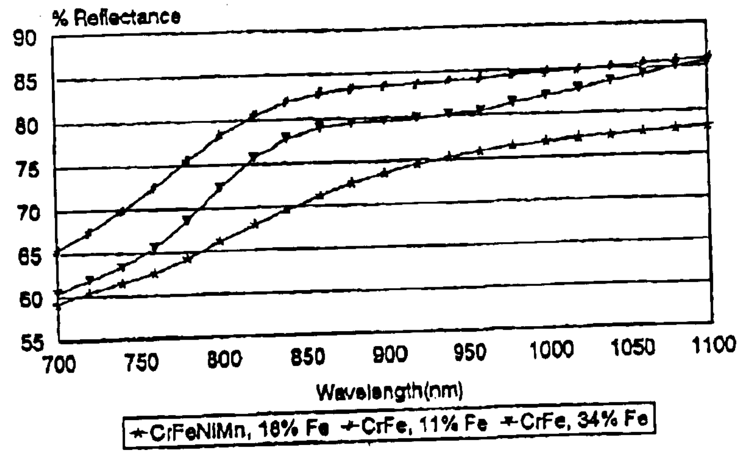

Figure 9

Med.Beige Heat Build-up Results

Temp.(Deg. C) vs. Time(min.)

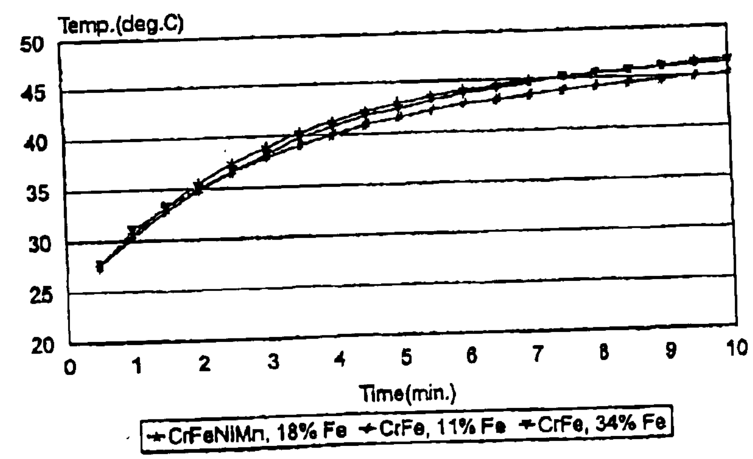

Figure 10

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IR Reflectance - Dark Beiges

IR Reflectance(%) vs. Wavelength(nm)

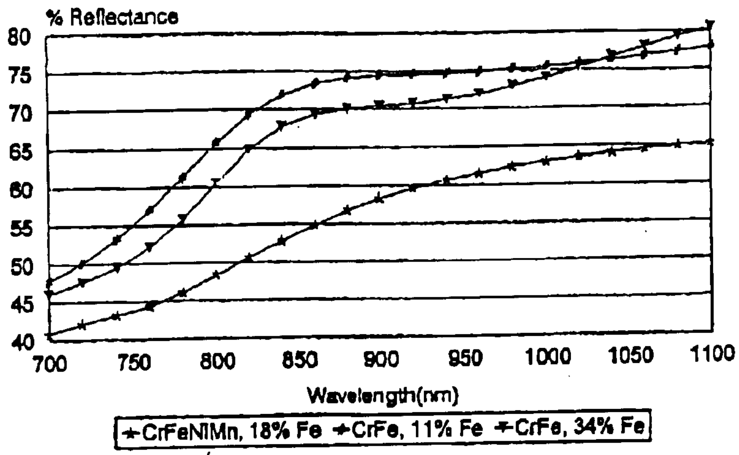

Figure 11

Dark Beige Heat Build-up Results

Temp.(Deg. C) vs. Time(min.)

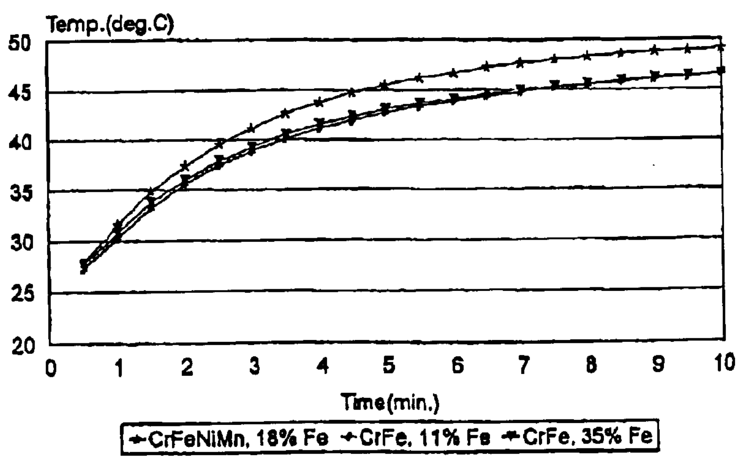

Figure 12

Black Pigment Weathering

S. Florida - 1 year

	CrFeNiMn(17%Fe)	CrFe(11%Fe)	CrFe(34%Fe)
1phr Pigment : 8.5phr TiO2	Avg. L* = 67.7	Avg. L* = 70.8	Avg. L* = 65.4
Delta L*	1.63	2.81	3.49
Delta a*	-0.27	-0.37	-0.74
Delta b*	1.35	0.73	1.13
Delta E	2.18	2.93	3.74

CIELAB Ill. D65 @ 10deg., SCI

Figure 13

Average Weathering Results

S. Florida - 1 year

		CrFeNiMn(17% Fe)	CrFe(11% Fe)	CrFe(34% Fe)
Light Beige:				
	Delta L*	0.41	0.48	0.41
	Delta a*	0	-0.02	-0.03
	Delta b*	0.38	0.37	0.44
	Delta E	0.61	0.63	0.63
Medium Beige:				
	Delta L*	1.02	1.62	1.47
	Delta a*	-0.02	-0.16	-0.17
	Delta b*	-0.41	-0.56	-0.56
	Delta E	1.25	1.72	1.53
Dark Beige:				
	Delta L*	1.52	2.48	1.88
	Delta a*	-0.06	-0.31	-0.2
	Delta b*	0.02	-0.45	-0.04
	Delta E	1.52	2.54	1.77

CIELAB Ill. D65 @ 10deg., SCI

Figure 14

[redacted]

Avg. Fe Content - in phr

Pigment	Lgt. Beige	Med. Beige	Dk. Beige
C.I. Pig. Black 30(18% Fe)	0.007	0.031	0.134
C.I. Pig. Green 17(11% Fe)	0.008	0.041	0.158
C.I. Pig. Green 17(34% Fe)	0.015	0.078	0.281

Figure 15

Avg. Black Pigment Content - in phr

Pigment	Lgt. Beige	Med. Beige	Dk. Beige
C.I. Pig. Black 30(18% Fe)	0.04	0.173	0.744
C.I. Pig. Green 17(11% Fe)	0.072	0.373	1.436
C.I. Pig. Green 17(34% Fe)	0.043	0.229	0.825

Figure 16

[redacted]

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General Information:

Materials/Pigments:

R-PVC Compound - Tin Mercaptide Stabilized Compound

Titanium Dioxide - Industry standard, encapsulated rutile grade

Pigment Brown 24 - CrSbTi, rutile structure

Pigment Yellow 164 - MnSbTi, rutile structure

IR Reflecting Blacks:

Pigment Black 30 - CrFeNiMn, spinel structure - approx. 18% as Fe

Pigment Green 17 - CrFe, Hematite structure - approx. 11% as Fe

Pigment Green 17 - CrFe, Hematite structure - approx. 34% as Fe

Colorimetric Values of Standard Shades:

	L*	a*	b*	C	H
Light Beige	87.5	-0.2	7.8	7.8	91.7
Medium Beige	76.5	0.7	11.4	11.4	86.3
Dark Beige	64.9	1.2	10.1	10.2	83.5

Color Measurement:(for all readings)

CIELAB Illuminant D65 @ 10°, Spectral Component Included

Weathering:

Test Method: ASTM #G7-89 - mounted at 45° facing due South
Location: Miami, FL
Start Date: March 3, 1995

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